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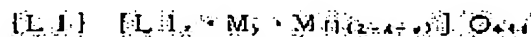
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(54) LITHIUM MANGANESE-BASED OXIDE, HAVING SPINEL STRUCTURE AND CONTAINING ANOTHER KIND OF ELEMENT, ITS PRODUCTION AND USE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To suppress the elution of Mn in an organic electrolytic solution of a lithium secondary battery by using a lithium manganese-based oxide having a spinel structure of a specific chemical composition containing at least another kind of element other than Li and Mn as a material of a positive electrode.

SOLUTION: This lithium manganese-based oxide having a spinel structure is represented by the formula [the interior of { } denotes the position of an oxygen tetrahedron in the structure; the interior of [ ] denotes the position of an oxygen octahedron in the structure;  $0 < (x) \leq 0.33$ ;  $0 < (y) \leq 1$ ;  $-0.5 < (d) < 0.8$ ] and contains at least another element (M) other than Li and Mn. The crystal structure is a cubic crystal and the lattice constant (a) is  $\geq 8.19$  and  $\leq 8.24$  Å. The other element M is selected from Be, Mg, Ca, Y, Ti, V, Cr, Fe, Cu, B, Al, Si, Pb, P and the like. Furthermore, the oxide preferably has 1-50 μm average agglomerated particle diameter, 0.1-5 m<sup>2</sup>/g BET specific surface area and  $\leq 3$  μm average primary particle diameter. The lithium manganese-based oxide containing the other element is produced by mixing respective compounds of the Mn, Li and the other element and baking the resultant mixture.



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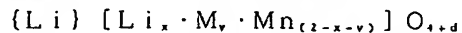
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(54) 【発明の名称】 他種元素を含有するスピネル構造リチウムマンガン系酸化物およびその製造方法並びにその用途

(57) 【要約】 (修正有)

【課題】 Li 二次電池用の正極材料として、有機電解液中でのMn 溶出を抑制した高性能なスピネル構造リチウムマンガン系酸化物および該リチウムマンガン系酸化物を正極に用いた高性能なリチウム二次電池を提供する。

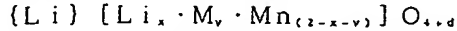
【解決手段】 以下の組成で表され、Li およびMn 以外の少なくとも1 種類他種元素 (M) を含有するスピネル構造リチウムマンガン系酸化物。



(ただし、{ } 内は構造中の酸素四面体位置、[ ] 内は構造中の酸素八面体位置を表す。0 < x ≤ 0.33, 0 < y ≤ 1.0, -0.5 < d < 0.8, M はLi およびMn 以外の元素)。

## 【特許請求の範囲】

【請求項1】以下の組成で表され、LiおよびMn以外の少なくとも1種類の他種元素(M)を含有するスピネル構造リチウムマンガン系酸化物。



(ただし、{ }内は構造中の酸素四面体位置、[ ]内は構造中の酸素八面体位置を表す。 $0 < x \leq 0.33$ ,  $0 < y \leq 1.0$ ,  $-0.5 < d < 0.8$ , MはLiおよびMn以外の元素)

【請求項2】結晶構造が立方晶であり、その格子定数aが、8.19オングストローム以上、8.24オングストローム以下である請求項1記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物。

【請求項3】該M元素は、Be, Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Fe, Co, Ni, Cu, Ag, Zn, B, Al, Ga, In, Si, Ge, Sn, Pb, P, As, SbおよびBiの群から選択された少なくとも1種の元素であることを特徴とする請求項1および2記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物。

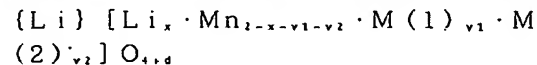
【請求項4】平均凝集粒子径が1~50 $\mu$ mであり、BET比表面積が0.1~5m<sup>2</sup>/gであることを特徴とする請求項1~3記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物。

【請求項5】平均一次粒子径が3 $\mu$ m以下であることを特徴とする請求項1~4記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物。

【請求項6】MがCrであることを特徴とする請求項1~5記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物。

【請求項7】請求項6において、 $0 < x \leq 0.15$ ,  $0.02 \leq y \leq 0.2$ であることを特徴とする他種元素を含有するスピネル構造リチウムマンガン系酸化物。

【請求項8】請求項1~5に記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物において、LiおよびMn以外の他種元素Mが2種類の元素(M(1), M(2))であり、下記の式で表される他種元素を含有するスピネル構造リチウムマンガン系酸化物。



(ただし、{ }内は構造中の酸素四面体位置、[ ]内は構造中の酸素八面体位置を表す。 $0 < x \leq 0.33$ ,  $0 < y_1 + y_2 \leq 1.0$ ,  $-0.5 < d < 0.8$ )

【請求項9】含有する他種元素の1種M(1)がCrであることを特徴とする請求項8記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物。

【請求項10】含有する他種元素のうちM(1)がCrであり、M(2)が遷位金属であることを特徴とする請求項8および9記載の他種元素を含有するスピネル構造

リチウムマンガン系酸化物。

【請求項11】含有する他種元素のうちM(1)がCrであり、M(2)がFeであることを特徴とする請求項8~10記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物。

【請求項12】 $0 < x \leq 0.15$ ,  $0 < y_1 \leq 0.2$ ,  $0 < y_2 \leq 0.2$ であることを特徴とする請求項11記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物。

【請求項13】マンガン化合物とリチウム化合物と含有他種元素の化合物を混合、焼成することにより他種元素を含有するスピネル構造リチウムマンガン系酸化物を製造する方法において、原料マンガン化合物として平均凝集粒子径が0.5~50 $\mu$ mであるマンガン酸化物を用いることを特徴とする請求項1~12記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物の製造方法。

【請求項14】請求項13記載の原料マンガン化合物の成形密度が2.7g/cm<sup>3</sup>以上であることを特徴とする他種元素を含有するスピネル構造リチウムマンガン系酸化物の製造方法。

【請求項15】請求項13および14記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物の製造方法において、原料マンガン化合物に含まれるNa, K量が500ppm以下であることを特徴とする他種元素を含有するスピネル構造リチウムマンガン系酸化物の製造方法。

【請求項16】請求項13~15に記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物の製造方法において、原料リチウム化合物のBET比表面積が1m<sup>2</sup>/g以上であることを特徴とする他種元素を含有するスピネル構造リチウムマンガン系酸化物の製造方法。

【請求項17】請求項16に記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物の製造方法において、原料リチウム化合物として炭酸リチウムを用いることを特徴とする他種元素を含有するスピネル構造リチウムマンガン系酸化物の製造方法。

【請求項18】請求項13~17に記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物の製造方法において、焼成温度が500~1000℃であり、焼成雰囲気が大気中であることを特徴とする他種元素を含有するスピネル構造リチウムマンガン系酸化物の製造方法。

【請求項19】請求項13~18に記載の他種元素を含有するスピネル構造リチウムマンガン系酸化物の製造方法において、マンガン化合物とリチウム化合物と含有他種元素の化合物を混合した後、造粒してから焼成することを特徴とする他種元素を含有するスピネル構造リチウムマンガン系酸化物の製造方法。

【請求項20】正極、負極、Liを含む電解質を溶解し

た非水電解液およびセバレーターからなるLi二次電池において、請求項1～12記載の他種元素を含有スピネル構造リチウムマンガン系酸化物を正極活物質として使用することを特徴とするLi二次電池。

【請求項21】請求項20のLi二次電池において、電気化学的にリチウムイオンを挿入・脱離する炭素系材料を負極活物質とすることを特徴とするLi二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明はLiおよびMn以外の他種元素(M)を含有するスピネル構造リチウムマンガン系酸化物およびその製造方法並び用途に関するものである。

【0002】マンガン酸化物は、電池活物質として、古くから使用されている材料である。マンガンとリチウムの複合物質であるリチウムマンガン酸化物は、および該リチウムマンガン酸化物のマンガンの一部を他種元素と置換したリチウムマンガン系酸化物は、高出力、高エネルギー密度が達成できるリチウム二次電池の正極活物質として、近年注目されている材料である。

【0003】

【従来の技術】リチウム二次電池用の正極材料は、電圧作動領域が高いこと、高放電容量であることおよびサイクル安定性が高いことが求められ、Liと各種金属、例えば、Co、Ni、Mn等、の複合酸化物が検討されている。

【0004】LiとMnの複合酸化物の一種であるスピネル構造のLiMn<sub>2</sub>O<sub>4</sub>は、放電時に4V付近および3V付近に平坦部部分のある二段放電を示すことが知られ、4V付近の作動領域で可逆的にサイクルさせることができれば、高いエネルギーを取り出すことが期待できるため、正極活物質として有望であると考えられている。

【0005】しかしながら、近年、LiMn<sub>2</sub>O<sub>4</sub>構造中のMnが、リチウム二次電池正極として充放電を行うと、有機電解液中で溶出することがわかった。さらに、本発明者らの実験では、電解液系の種類にもよるが、充放電を行わなくとも、有機電解液中でLiMn<sub>2</sub>O<sub>4</sub>を85℃で保存しただけでも構造中のMn量が1mol%程度も溶出し、溶出後には正極材料としての特性が著しく低下することがわかった。

【0006】これは、LiMn<sub>2</sub>O<sub>4</sub>をリチウム二次電池用正極として使用した場合、充放電を行わなくとも、長期間保存しただけで、構造中のMnが有機電解液中で溶出し、リチウム二次電池用正極として作動しなくなる可能性を示している。

【0007】

【発明が解決しようとする課題】本発明の目的は、Li二次電池用の正極材料として、有機電解液中でのMn溶出を抑制した高性能なスピネル構造リチウムマンガン系

酸化物および該リチウムマンガン系酸化物を正極に用いた高性能なリチウム二次電池を提供することにある。

【0008】

【課題を解決するための手段】本発明者らは鋭意検討した結果、以下の組成で表され、LiおよびMn以外の多種元素を含有するスピネル構造リチウムマンガン系酸化物が上記目的を達成できることを見いだした。

【0009】

{Li}[Li<sub>x</sub>·M<sub>y</sub>·Mn<sub>(2-x-y)</sub>]O<sub>4</sub>

(ただし、{}内は構造中の酸素四面体位置(8aサイト)、[]内は構造中の酸素八面体位置(16dサイト)を表す。0<x≤0.33, 0<y≤1.0, -0.5<d<0.8)。

【0010】このd値は、焼成雰囲気還元性雰囲気であれば、マイナスの値となり、酸化性雰囲気ではプラスの値となる。MはLiおよびMn以外の元素である。

【0011】さらに、本発明のLiおよびMn以外の他種元素(M)を含有するスピネル構造リチウムマンガン系酸化物の製造方法および本発明のLiおよびMn以外の他種元素(M)を含有するスピネル構造リチウムマンガン系酸化物を正極活物質として用いた高性能なリチウム二次電池を見出し、本発明を完成した。

【0012】

【作用】以下、本発明を具体的に説明をする。

【0013】本発明のLiおよびMn以外の他種元素(M)を含有するスピネル構造リチウムマンガン系酸化物は以下の組成である。

【0014】

{Li}[Li<sub>x</sub>·M<sub>y</sub>·Mn<sub>(2-x-y)</sub>]O<sub>4</sub>

(ただし、{}内は構造中の酸素四面体位置、[]内は構造中の酸素八面体位置を表す。0<x≤0.33, 0<y≤1.0, -0.5<d<0.8, MはLiおよびMn以外の元素)

該M元素は、構造中の酸素四面体位置に存在し、生成物として結晶構造が立方晶のスピネル構造であり、その格子定数aが、8.19オングストローム以上、8.24オングストローム以下であるスピネル構造リチウムマンガン系酸化物を形成するものが好ましい。

【0015】尚、立方晶以外のスピネル構造としては、正方晶等があるが、作動電位が低くなり、Li二次電池を構成した場合に取り出されるエネルギーが小さくなり好ましくない。

【0016】また、その格子定数aが上記範囲外となると、その構造中のマンガンが不安定となるため、Mn溶出量が大きくなり好ましくない。

【0017】該M元素は、Be、Mg、Ca、Sr、Ba、Sc、Y、Ti、Zr、V、Nb、Ta、Cr、Mo、W、Fe、Co、Ni、Cu、Ag、Zn、B、Al、Ga、In、Si、Ge、Sn、Pb、P、As、SbおよびBiの群から選択された少なくとも1種の元

素である。

【0018】さらに本発明の他種元素を含有するスピネル構造リチウムマンガン系酸化物の平均凝集粒子径が1～50μmであり、且つ、BET比表面積が0.1～5m<sup>2</sup>/gであることが好ましい。

【0019】平均凝集粒子径が該範囲より大きい場合、またはBET比表面積が該範囲より小さい場合には、製造に高温が必要であり、また、電池活物質に使用した場合に高い性能が得られにくいため好ましくなく、逆に平均凝集粒子径が該範囲より小さい場合、またはBET比表面積が該範囲より大きい場合には、電池活物質に使用する場合に充填性が悪く、また構造中からMnが溶出しやすい等の問題が生じやすく好ましくない。

【0020】また、本発明の他種元素を含有するスピネル構造リチウムマンガン系酸化物の平均一次粒子径は3μm以下であることが好ましい。該範囲より大きい場合、電池活物質などに使用した場合に高い性能が得られにくいため好ましくない。

【0021】本発明の他種元素を含有するスピネル構造リチウムマンガン系酸化物の他種元素の量を表すyは、0<y≤1.0であり、2種以上の他種元素を含有する場合には、各他種元素の含有量をy<sub>1</sub>, y<sub>2</sub>, y<sub>3</sub>・・・y<sub>n</sub>とし、0<y<sub>1</sub>+y<sub>2</sub>+y<sub>3</sub>+・・・+y<sub>n</sub>≤1.0である。

【0022】該yのトータル量が1.0以上では充放電容量が少なくなり、好ましくない。本発明の他種元素を含有するスピネル構造リチウムマンガン系酸化物中のLiは構造中の酸素四面体位置と酸素八面体位置の両方に存在し、酸素四面体位置に存在する量を1とした場合の酸素八面体位置に存在する量xは0<x≤0.33である。

【0023】Liの総量が1未満の場合、スピネル構造の単相構造が得られないか、又は、有機電解液中へのMnの溶出量が大きくなり好ましくなく、該範囲よりも大きい場合も、充放電容量が小さくなり好ましくない。

【0024】該xの値は0≤x≤0.15の場合、容量が大きく取れ、且つ、Mn溶出量が低く抑えられ、特に好ましい。

【0025】本発明のLiおよびMn以外の元素が1種の場合にはCrが好ましい。

【0026】他種元素がCrの場合には、その組成式は以下ようになる。

【0027】

{Li}[Li<sub>x</sub>・Mn<sub>2-x-y</sub>・Cr<sub>y</sub>]O<sub>4.4</sub>

(ただし、{ }内は構造中の酸素四面体位置、[ ]内は構造中の酸素八面体位置を表す。0<x≤0.33, 0<y≤1.0, -0.5<d<0.8)

この場合、0<x≤0.15, 0.02≤y≤0.2であることが好ましい。さらに、LiおよびMn以外の他種元素を2種(M(1), M(2))を含有する場合

は、下記の式で表される。

【0028】{Li}[Li<sub>x</sub>・Mn<sub>2-x-y<sub>1</sub>-y<sub>2</sub></sub>・M(1)<sub>y<sub>1</sub></sub>・M(2)<sub>y<sub>2</sub></sub>]O<sub>4.4</sub>

(ただし、{ }内は構造中の酸素四面体位置、[ ]内は構造中の酸素八面体位置を表す。0<x≤0.33, 0<y<sub>1</sub>+y<sub>2</sub>≤1.0, -0.5<d<0.8, M(1)およびM(2)はLiおよびMn以外の元素)含有する他種元素の1種M(1)がCrであることが好ましく、M(2)は遷位金属であることが好ましい。

【0029】特に含有する他種元素のうちM(1)がCrであり、M(2)がFeであることはより好ましく、その場合には下記の式で表される。

【0030】{Li}[Li<sub>x</sub>・Cr<sub>y<sub>1</sub></sub>・Fe<sub>y<sub>2</sub></sub>・Mn<sub>2-x-y<sub>1</sub>-y<sub>2</sub></sub>]O<sub>4.4</sub>(ただし、{ }内は構造中の酸素四面体位置、[ ]内は構造中の酸素八面体位置を表す。0<x≤0.33, 0<y<sub>1</sub>≤0.5, 0<y<sub>2</sub>≤0.5, -0.5<d<0.8)

該組成式において0<x≤0.15, 0<y<sub>1</sub>≤0.2, 0<y<sub>2</sub>≤0.2であることが好ましい。

【0031】以上のように本発明の他種元素を含有スピネル構造リチウムマンガン系酸化物は構造中の酸素四面体位置にLiを酸素八面体位置にLiとMnとさらにLiおよびMn以外の少なくとも1種類の他種元素(M)を含有するスピネル構造リチウムマンガン系酸化物であり、さらには、電池活物質またはLi吸着材などに使用した場合に高性能となる粒子構造をもつものである。

【0032】前述の本発明の他種元素を含有スピネル構造リチウムマンガン系酸化物は、マンガン化合物とリチウム化合物と含有他種元素の化合物を混合、焼成することにより製造方法できる。

【0033】混合する化合物は酸化物、水酸化物、酸化水酸化物、炭酸塩、塩化物塩、硝酸塩および硫酸塩等のなかで焼成温度以下で酸化物を生成できるものであればよいが、特に、酸化物、水酸化物、酸化水酸化物、炭酸塩は反応性、廃ガスの環境へあたえる影響から好ましい。

【0034】原料マンガン化合物として平均凝集粒子径が0.5～50μmであるマンガン酸化物を使用することが必須であり、その原料マンガン化合物の成形密度が2.7g/cm<sup>3</sup>以上であるものをを用いることが好ましい。

【0035】該範囲外のマンガン酸化物を用いることは本発明の他種元素を含有するスピネル構造リチウムマンガン系酸化物の粉体特性を満足するものを得ることが難しいため好ましくない。

【0036】さらに原料マンガン化合物に含まれるNa, K量が500ppm以下であるものをを用いるのが好ましく、該Na, K量が多いと生成物を電池活物質に使用した場合に高性能なLi二次電池を作成することが難しい。

【0037】本発明の他種元素を含有するスピネル構造リチウムマンガン系酸化物の製造方法においては、原料リチウム化合物としてBET比表面積が $1\text{ m}^2/\text{g}$ 以上であるリチウム化合物を用いることが好ましい。

【0038】リチウム化合物としては炭酸塩、硝酸塩、塩化物塩、水酸化物、酸化物等が例示され、特にBET比表面積が $1\text{ m}^2/\text{g}$ 以上である炭酸リチウムを用いれば、大気中でも容易に均一な他種元素を含有するスピネル構造リチウムマンガン系酸化物が製造でき非常に好ましい。

【0039】本発明の他種元素を含有スピネル構造リチウムマンガン系酸化物の製造における焼成温度は $500\sim 1000^\circ\text{C}$ の範囲から所望の粉体特性が得られるように適宜選択される。

【0040】焼成温度が該範囲外であると、生成物のBET比表面積および/または一次粒子径が所望の範囲となり難く好ましくない。

【0041】焼成時の雰囲気は、大気中及び酸素リッチ雰囲気の両方共、使用可能であるが、焼成炉の構造の容易さから、大気中が好ましい。

【0042】前記の製造条件において、次に示す方法を採用することが特に好ましい。

【0043】1. マンガン化合物とリチウム化合物及び他種元素の化合物を混合してから造粒した後、焼成する方法。

【0044】2. マンガン化合物とリチウム化合物とを混合、造粒、焼成した後、リチウム化合物および/または含有他種元素の化合物を混合、造粒した後、焼成する方法。

【0045】3. マンガン化合物、リチウム化合物及び含有他種元素の化合物を混合、造粒、焼成した後、マンガン化合物、リチウム化合物及び含有他種元素の化合物のいずれか1種を混合し造粒した後、焼成する。

【0046】さらに、原料を混合する場合均一にすることができれば、通常の方法のいかなる方法も採用でき、ロータリーキルン等のように混合しながら焼成することも好適である。

【0047】製造したスピネル構造リチウムマンガン系酸化物は適時、粉碎、分級を行うのが好ましい。

【0048】本発明では、前述のようにして製造したスピネル構造リチウムマンガン系酸化物を正極活物質として用いたLi二次電池を作製した。

【0049】本発明のリチウム二次電池で用いる負極活物質には、金属リチウム並びにリチウムまたはリチウムイオンを吸蔵放出可能な物質を用いることができる。例えば、金属リチウム、リチウム/アルミニウム合金、リチウム/スズ合金、リチウム/鉛合金および電気化学的にリチウムイオンを挿入・脱離する炭素系材料が例示され、電気化学的にリチウムイオンを挿入・脱離する炭素系材料が安全性および電池の特性の面から特に好適であ

る。

【0050】また、本発明のリチウム二次電池で用いる電解質としては、特に制限はないが、例えば、カーボネート類、スルホラン類、ラクトン類、エーテル類等の有機溶媒中にリチウム塩を溶解したものや、リチウムイオン導電性の固体電解質を用いることができる。

【0051】本発明のスピネル構造リチウムマンガン系酸化物を正極活物質に用いて、図1に示す電池を構成した。

10 【0052】図中において、1：正極用リード線、2：正極集電用メッシュ、3：正極、4：セパレータ、5：負極、6：負極集電用メッシュ、7：負極用リード線、8：容器を示す。

【0053】本発明では、以上述べてきた正極活物質、負極活物質およびリチウム塩含有非水電解質を用いて、安定な高性能なリチウム二次電池を得ることができる。

【0054】以下実施例を述べるが、本発明はこれに限定されるものではない。

【0055】

20 【実施例】本発明の実施例および比較例における各測定は、以下の条件で実施した。

【0056】・XRDパターンは以下の条件で測定した。

【0057】

測定機種：マックサイエンス社 MXP-3

照射X線：Cu K $\alpha$ 線

測定モード：ステップスキャン

スキャン条件：毎秒0.04度

計測時間：3秒

30 測定範囲： $2\theta$ として5度から80度

・組成分析はICP分光法で行った。

【0058】・Mn元素の酸化度はしゅう酸法で行った。

【0059】『スピネル構造リチウムマンガン系酸化物の合成』実施例および比較例として、以下の方法で合成した。

【0060】実施例1～5

他種元素MとしてCrを使用し、平均凝集粒子径が $20\mu\text{m}$ の $\text{MnO}_2$ （東ソー株式会社製電解二酸化マンガン）とBET比表面積が $3\text{ m}^2/\text{g}$ の炭酸リチウム（ $\text{Li}_2\text{CO}_3$ ）と平均凝集粒子径が $1\mu\text{m}$ の酸化クロム（ $\text{Cr}_2\text{O}_3$ ）をCrとMnの比率を変化させ、以下の組成式においてLi量をxの値が0.06（ $\text{Li}:(\text{Li}+\text{Mn}+\text{Cr})=1.06:3.00$ ）で一定になるように秤量し、乳鉢でよく混合した後、 $450^\circ\text{C}$ で24時間仮焼した後、 $750^\circ\text{C}$ で24時間焼成した。

【0061】

$[\text{Li}_{0.06}\cdot\text{Cr}_x\cdot\text{Mn}_{(3.00-x)}]\text{O}_4$

50 実施例3で得られたスピネル構造リチウムマンガン系酸化物の粒子構造をSEMを用い、20,000倍の倍率

で観察した写真を図2に示す。

【0062】この図から、実施例3で得られたスピネル構造リチウムマンガン系酸化物の全ての粒子一次粒子径が1μm以下であり、平均一次粒子径が1μm以下であることが明らかとなった。

【0063】又、得られたスピネル構造リチウムマンガン系酸化物の構造が上記の化学式であることを、X線回折による格子定数値及びRietveld分析により推定した。

#### 【0064】実施例6

実施例3において、最終の焼成温度を750℃から900℃に高くした以外は同一とした。

【0065】得られたスピネル構造リチウムマンガン系酸化物の粒子構造をSEMを用い、20,000倍の倍率で観察した写真を図3に示す。

【0066】この図から、得られたスピネル構造リチウムマンガン系酸化物の一次粒子径が1μm以上の粒子も含まれるいるが、平均一次粒子径は3μm以下であることが明らかとなった。

#### 【0067】実施例7

実施例4においてLi量をxの値が0.02になるようにした以外は同一とした。

#### 【0068】実施例8～10

実施例2～4においてCrのかわりにCoを使用した以外は同一とした。

【0069】なお、Co原料は塩基性炭酸コバルトを使用した。

#### 【0070】実施例11～13

実施例2～4においてCrのかわりにNiを使用した以外は同一とした。

【0071】なお、Ni原料は塩基性炭酸ニッケルを使用した。

#### 【0072】実施例14～16

実施例2～4においてCrのかわりにFeを使用した以外は同一とした。

【0073】なお、Fe原料はFe<sub>2</sub>O<sub>3</sub>を使用した。

#### 【0074】実施例17

第一の他種元素M1としてCrを、第二の他種元素M2としてFe使用し、下記組成式において、Li量をxの

値が0.01(Li:(Li+Mn+Cr+Fe)=1.01:3.00)、y1の値が0.1、y2の値が0.1になるように凝集粒子径が20μmのMnO<sub>2</sub>、BET比表面積が3m<sup>2</sup>/gであるLi<sub>2</sub>CO<sub>3</sub>、平均凝集粒子径1μmのCr<sub>2</sub>O<sub>3</sub>及びFe<sub>2</sub>O<sub>3</sub>を秤量し、乳鉢でよく混合した後、450℃で24時間仮焼した後、750℃で24時間焼成した。  
(Li)<sub>1-x</sub>[Li<sub>0.01</sub>·Cr<sub>0.1</sub>·Fe<sub>0.1</sub>·Mn<sub>1.7</sub>]<sub>y1</sub>O<sub>y2</sub>

#### 比較例1

10 凝集粒子径が20μmのMnO<sub>2</sub>(東ソー株式会社製電解二酸化マンガン)とBET比表面積が3m<sup>2</sup>/gである炭酸リチウムをx=0.0(Li:Mn=1.00:2.0)となるように秤量し、乳鉢でよく混合した後、450℃で24時間仮焼した後、750℃で24時間焼成した。

【0075】生成物はJCPDSカード35-782のLiMn<sub>2</sub>O<sub>4</sub>と同様のパターンを示した。

#### 【0076】比較例2

比較例1でx=0.06(Li:Li+Mn=1.06:3.0)とした以外は比較例1と同一の条件で行った。

#### 【0077】比較例3

比較例1でx=0.10(Li:Li+Mn=1.10:3.0)とした以外は比較例1と同一の条件で行った。

#### 【0078】比較例4

Li:Cr:Mn=0.95:0.2:1.80となるように混合し、比較例1の条件で焼成した。

【0079】実施例および比較例の生成物は比較例4以外は立方晶のスピネル構造単相であった。

30 【0080】『Mn溶出試験』実施例および比較例で作製したリチウムマンガン系酸化物を各3gを六フッ化リン酸リチウムを1mol/dm<sup>3</sup>の濃度でエチレンカーボネートとジメチルカーボネートの混合溶媒に溶解した電解液15mlに含浸し、85℃、100時間保持した後、電解液中のMn量をICP分光法により分析した。

【0081】結果を表1に示した。

【0082】

【表1】



	Li量 (x)	他種元素		Mn溶出量 (mol%)	格子定数 (Å)	BET ( $m^2/g$ )	初期容量 (mAh/g)	容量維持率(%) 室温 50℃	溶出試験維持率 (%)
		M	y						
実施例1	0.06	Cr	0.01	0.65	8.237	1.75	120	-- --	--
実施例2	0.06	Cr	0.02	0.49	8.235	1.58	120	-- --	--
実施例3	0.06	Cr	0.1	0.09	8.230	2.31	108	99 94	90
実施例4	0.06	Cr	0.2	0.11	8.223	1.83	94	99 95	95
実施例5	0.06	Cr	0.4	0.14	8.209	1.80	63	97 95	95
実施例6	0.06	Cr	0.1	0.07	8.237	0.90	103	99 94	90
実施例7	0.02	Cr	0.2	0.20	8.242	2.11	115	95 90	85
実施例8	0.06	Co	0.02	0.64	8.231	1.41	120	-- --	--
実施例9	0.06	Co	0.1	0.52	8.228	1.60	108	96 91	81
実施例10	0.06	Co	0.2	0.49	8.196	1.43	93	96 92	85
実施例11	0.06	Ni	0.02	0.62	8.234	1.56	117	-- --	--
実施例12	0.06	Ni	0.1	0.23	8.219	1.73	93	95 92	88
実施例13	0.06	Ni	0.2	0.13	8.202	1.86	63	96 92	90
実施例14	0.06	Fe	0.02	0.49	8.235	1.68	120	90 83	81
実施例15	0.06	Fe	0.1	0.31	8.237	2.11	108	92 90	85
実施例16	0.06	Fe	0.2	0.18	8.234	2.12	93	99 95	96
実施例17	0.01	Cr	0.1	0.05	8.239	1.88	107	99 95	94
		Fe	0.1						
比較例1	1.00	--	0.0	1.06	8.242	1.80	130	90 60	60
比較例2	1.06	--	0.0	0.84	8.234	1.75	123	94 83	75
比較例3	1.10	--	0.0	0.83	8.219	1.62	106	95 84	76
比較例4	0.95	Cr	0.2	0.95	---	1.70	---	-- --	--

【0083】「電池の構成」実施例および比較例で得られたリチウムマンガン系酸化物および前記Mn溶出試験後の試料を用いて電池試験を行った。電池試験は試料と導電剤のポリテトラフルオロエチレンとアセチレンブラックの混合物（商品名：TAB-2）を、重量比で2：1の割合で混合した。混合物を1ton/cm<sup>2</sup>の圧力で、メッシュ（SUS 316）上にペレット状に成形した後、200℃で24時間減圧乾燥した。

【0084】この様にして得られたペレットを図1の3の正極に用い、図1の5の負極にはリチウム箔（厚さ0.2mm）から切り抜いたリチウム片を用い、電解液には六フッ化リン酸リチウムを1mol/dm<sup>3</sup>の濃度でプロピレンカーボネートとジエチルカーボネートの混合溶媒に溶解した溶液を図1の4のセパレーターに含浸させ、また、負極に電気化学的にリチウムイオンを挿入・脱離する炭素系材料を使用して図1に示した電池を構成した。

【0085】「電池特性の評価」実施例および比較例で作製したリチウムマンガン系酸化物を正極活物質に用いて電池を作製し、1.0mA/cm<sup>2</sup>の一定電流で、電池電圧が4.5Vから3.5Vの間で充放電を繰り返した。

【0086】試験温度は室温と50℃で実施した。

【0087】表1に初期容量、容量維持率（10サイク

ル目に対する50サイクル目の放電容量の%）および溶出試験維持率（溶出試験後の容量の溶出試験前の初期容量に対する%）を示した。

【0088】

【発明の効果】本発明のスピンネル構造リチウムマンガン系酸化物は、有機溶媒中でMn溶出が少なく、長期保存後も安定した充放電サイクル性を発揮し、さらに高温で充放電を行っても劣化が少ない。

【図面の簡単な説明】

【図1】本発明のスピンネル構造リチウムマンガン系酸化物を正極活物質に用いて構成した電池を示す。

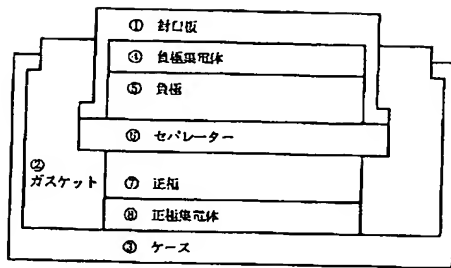
【符号の説明】

- 1：正極用リード線
- 2：正極集電用メッシュ
- 3：正極
- 4：セパレーター
- 5：負極
- 6：負極集電用メッシュ
- 7：負極用リード線
- 8：容器

【図2】実施例3で得られたスピンネル構造リチウムマンガン系酸化物の粒子構造を示す写真である。

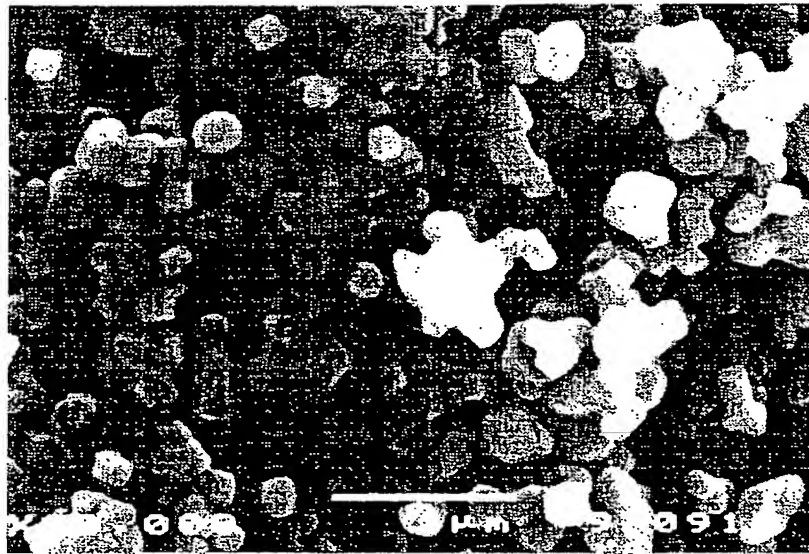
【図3】実施例6で得られたスピンネル構造リチウムマンガン系酸化物の粒子構造を示す写真である。

【図1】



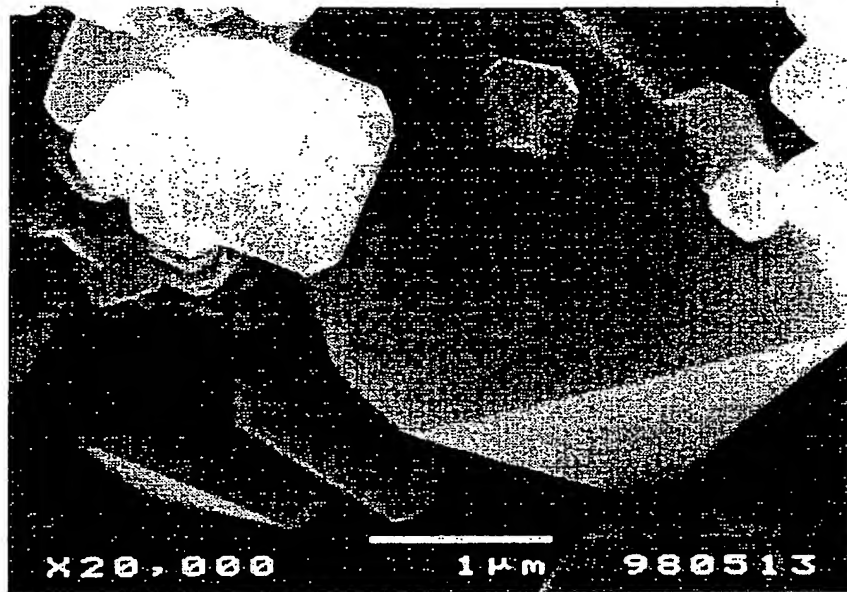
【図2】

図面代用写真



【図3】

図面代用写真



フロントページの続き

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION  
TECHNICAL PROBLEM MEANS OPERATION EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

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[Translation done.]

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## CLAIMS

[Claim(s)]

[Claim 1] The Spinel structure lithium manganese system oxide which is expressed with the following composition and contains at least one kind of other type elements other than Li and Mn (M).

{Li} [Lix-My-Mn(2-x-y)] O<sub>4+d</sub> (however, { } -- inside -- the oxygen tetrahedral site in structure, and [ ] -- inside expresses the oxygen octahedral site in structure)  $0 < x \leq 0.33$ ,  $0 < y \leq 1.0$ ,  $-0.5 < d < 0.8$ , and M are elements other than Li and Mn.

[Claim 2] The Spinel structure lithium manganese system oxide containing the other type element according to claim 1 the lattice constant a of whose the crystal structure is a cubic and is 8.19Å or more and 8.24Å or less.

[Claim 3] These M elements That they are at least one sort of elements chosen from the group of Be, Mg, calcium, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Fe, Co, nickel, Cu, Ag, Zn, B, aluminum, Ga, In, Si, germanium, Sn, Pb, P, As, Sb, and Bi The Spinel structure lithium manganese system oxide containing the other type element of the claim 1 and 2 publications by which it is characterized.

[Claim 4] The Spinel structure lithium manganese system oxide containing the other type element according to claim 1 to 3 characterized by for the diameter of an average floc being 1-50 micrometers, and a BET specific surface area being 0.1-5m<sup>2</sup>/g.

[Claim 5] The Spinel structure lithium manganese system oxide containing the other type element according to claim 1 to 4 characterized by the first [ an average of ] particle diameter being 3 micrometers or less.

[Claim 6] The Spinel structure lithium manganese system oxide containing the other type element according to claim 1 to 5 characterized by M being Cr.

[Claim 7] The Spinel structure lithium manganese system oxide containing the other type element characterized by being  $0 < x \leq 0.15$  and  $0.02 \leq y \leq 0.2$  in a claim 6.

[Claim 8] The Spinel structure lithium manganese system oxide containing the other type element which other type elements M other than Li and Mn are two kinds of elements (M (1), M (2)), and is expressed with the following formula in the Spinel structure lithium manganese system oxide containing an other type element according to claim 1 to 5.

Lix-Mn<sub>2-x-y1-y2</sub>, M(1) y<sub>1</sub>, and {Li} [M(2) y<sub>2</sub>] O<sub>4+d</sub> (however, { } -- inside -- the oxygen tetrahedral site in structure, and [ ] -- inside expresses the oxygen octahedral site in structure)  $0 < x \leq 0.33$ ,  $0 < y_1 + y_2 \leq 1.0$ ,  $-0.5 < d < 0.8$

[Claim 9] The Spinel structure lithium manganese system oxide containing the other type element according to claim 8 characterized by one sort [ of the other type element to contain ] M (1) being Cr.

[Claim 10] The Spinel structure lithium manganese system oxide containing the claim 8 characterized by for M (1) being Cr among the other type elements to contain, and M (2) being a \*\*\*\* metal, and the other type element of nine publications.

[Claim 11] The Spinel structure lithium manganese system oxide containing the other type element according to claim 8 to 10 characterized by for M (1) being Cr among the other type elements to contain, and M (2) being Fe.

[Claim 12] The Spinel structure lithium manganese system oxide containing the other type element according to claim 11 characterized by being  $0 < x \leq 0.15$ ,  $0 < y_1 \leq 0.2$ , and  $0 < y_2 \leq 0.2$ .

[Claim 13] The manufacture method of the Spinel structure lithium manganese system oxide containing the other type element according to claim 1 to 12 characterized by using the manganic acid ghost whose diameter of an average floc is 0.5-50 micrometers as a raw material manganese compound in the method of manufacturing the Spinel structure lithium manganese system oxide which contains an other type element by mixing and calcinating a manganese compound, a lithium compound, and the compound of a content other type element.

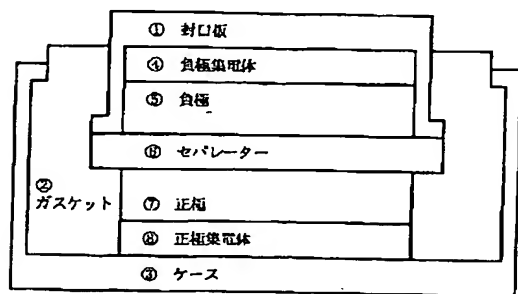

[Claim 14] The manufacture method of the Spinel structure lithium manganese system oxide containing the other type element characterized by the forming density of a raw material manganese compound according to claim 13 being three or more 2.7 g/cm.

[Claim 15] The manufacture method of the Spinel structure lithium manganese system oxide which contains Na

contained in a raw material manganese compound, and the other type element characterized by the amount of K being 500 ppm or less in the manufacture method of the Spinel structure lithium manganese system oxide containing a claim 13 and an other type element given in 14.

[Claim 16] The manufacture method of the Spinel structure lithium manganese system oxide which contains the other type element characterized by the BET specific surface area of a raw material lithium compound being more than  $1\text{m}^2/\text{g}$  in the manufacture method of the Spinel structure lithium manganese system oxide containing an other type element according to claim 13 to 15.

[Claim 17] The manufacture method of the Spinel structure lithium manganese system oxide containing the other type element characterized by using a lithium carbonate as a raw material lithium compound in the manufacture method of the Spinel structure lithium manganese system oxide containing an other type element according to claim 16.

Drawing selection drawing 1 

[Translation done.]

## \* NOTICES \*

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the Spinel structure lithium manganese system oxide containing other type elements other than Li and Mn (M), and its manufacture method list use.

[0002] A manganic acid ghost is a material used for many years as a cell active material. The lithium manganic acid ghost which is the quality of a composite of manganese and a lithium, and the lithium manganese system oxide which replaced some manganese of this lithium manganic acid ghost by the other type element are material which attracts attention in recent years as a positive active material of a lithium secondary battery which can attain high power and high-energy density.

[0003]

[Description of the Prior Art] It is called for that the positive-electrode material for lithium secondary batteries has high that a voltage operating space is high, that it is high service capacity, and cycle stability, and the multiple oxide of \*\*s, such as Li and various metals, for example, Co, nickel, Mn, etc., is examined.

[0004] If it is known that the two-step electric discharge with a flat part portion is shown and the 4V neighborhood and the 3V neighborhood can be made to carry out the cycle of  $\text{LiMn}_2\text{O}_4$  of the Spinel structure which is a kind of the multiple oxide of Li and Mn in reversible by the operating space of the 4V neighborhood at the time of electric discharge, since it can expect taking out high energy, it is thought that it is promising as a positive active material.

[0005] However, when Mn in  $\text{LiMn}_2\text{O}_4$  structure performed charge and discharge as a lithium secondary battery positive electrode, it turns out that it is eluted in the organic electrolytic solution in recent years. Furthermore, in the experiment of this invention persons, it was based on the kind of electrolytic-solution system, and having saved  $\text{LiMn}_2\text{O}_4$  at 85 degrees C in the organic electrolytic solution, even if it did not perform charge and discharge also turned out that the amount of Mn in structure was eluted also about 1mol%, and the property as a positive-electrode material fell remarkably after elution.

[0006] When  $\text{LiMn}_2\text{O}_4$  was used as a positive electrode for lithium secondary batteries, even if it did not perform charge and discharge, it only saved for a long period of time, and Mn in structure is eluted in the organic electrolytic solution, and this shows possibility of stopping operating as a positive electrode for lithium secondary batteries.

[0007]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the highly efficient lithium secondary battery which used for the positive electrode the highly efficient Spinel structure lithium manganese system oxide and this lithium manganese system oxide which suppressed Mn elution in the organic electrolytic solution as a positive-electrode material for Li rechargeable batteries.

[0008]

[Means for Solving the Problem] As a result of this invention persons' inquiring wholeheartedly, it was expressed with the following composition and the Spinel structure lithium manganese system oxide containing variety elements other than Li and Mn found out that the above-mentioned purpose could be attained.

[0009]

{Li} [Lix-My-Mn(2-x-y)]  $\text{O}_{4+d}$  (however, { } -- inside -- the oxygen tetrahedral site in structure (8a site), and [ ] -- inside expresses the oxygen octahedral site in structure (16d site))  $0 < x \leq 0.33$ ,  $0 < y \leq 1.0$ ,  $-0.5 < d < 0.8$ .

[0010] If a firing environments is a reducing atmosphere, this d value will turn into a value of minus, and will turn into a value of plus in an oxidizing atmosphere. M is elements other than Li and Mn.

[0011] Furthermore, the highly efficient lithium secondary battery using the Spinel structure lithium manganese system oxide containing the manufacture method of the Spinel structure lithium manganese system oxide containing Li of this invention and other type elements other than Mn (M), Li of this invention, and other type elements other than Mn (M) as a positive active material was found out, and this invention was completed.

[0012]



[Function] Hereafter, this invention is explained concretely.

[0013] The Spinel structure lithium manganese system oxides containing Li of this invention and other type elements other than Mn (M) are the following composition.

[0014] {Li} [Lix-My-Mn(2-x-y)] O<sub>4+d</sub> (however, { } -- inside -- the oxygen tetrahedral site in structure, and [] -- inside expresses the oxygen octahedral site in structure)  $0 < x \leq 0.33$ ,  $0 < y \leq 1.0$ ,  $-0.5 < d < 0.8$ , and M are elements other than Li and Mn.

It exists in the oxygen tetrahedral site in structure, the crystal structure is cubic Spinel structure as a product, and, as for these M elements, what forms the Spinel structure lithium manganese system oxide the lattice constant a of whose is 8.19Å or more and 8.24Å or less is desirable.

[0015] In addition, the energy taken out when action potential becomes low and constitutes Li rechargeable battery as Spinel structure other than a cubic, although there was a tetragonal phase etc. becomes small and is not desirable.

[0016] moreover, the lattice constant a -- the above -- if it becomes out of range, since the manganese in the structure will become unstable, Mn elution volume becomes large and is not desirable

[0017] These M elements are at least one sort of elements chosen from the group of Be, Mg, calcium, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Fe, Co, nickel, Cu, Ag, Zn, B, aluminum, Ga, In, Si, germanium, Sn, Pb, P, As, Sb, and Bi.

[0018] It is desirable that the diameter of an average floc of the Spinel structure lithium manganese system oxide which furthermore contains the other type element of this invention is 1-50 micrometers, and a BET specific surface area is 0.1-5m<sup>2</sup>/g.

[0019] When the diameter of an average floc is larger than this range, or when a BET specific surface area is smaller than this range An elevated temperature is required for manufacture, and since a high performance is hard to be obtained when it is used for a cell active material, are not desirable. Conversely, when the diameter of an average floc is smaller than this range, or when a BET specific surface area is larger than this range and it uses it for a cell active material, restoration nature is bad, and the problem of Mn tending to be eluted out of structure is easy to be generated and is not desirable.

[0020] Moreover, as for the first [ an average of ] particle diameter of the Spinel structure lithium manganese system oxide containing the other type element of this invention, it is desirable that it is 3 micrometers or less. Since a high performance is hard to be obtained when larger [ than this range ] and it is used for a cell active material etc., it is not desirable.

[0021] y showing the amount of the other type element of the Spinel structure lithium manganese system oxide containing the other type element of this invention is [ ... It is  $y_n \leq 1.0$ . ] the content of each other type element, when it is  $0 < y \leq 1.0$  and contains two or more sorts of other type elements y<sub>1</sub>, y<sub>2</sub>, and y<sub>3</sub> ... It is referred to as y<sub>n</sub> and is  $0 < y_1 + y_2 + y_3 + \dots$ .

[0022] this -- charge-and-discharge capacity of the total amount of y decreases, and it is not desirable at 1.0 or more The amount x which exists in the oxygen octahedral site at the time of setting to 1 the amount which Li in the Spinel structure lithium manganese system oxide containing the other type element of this invention exists in both the oxygen tetrahedral site in structure and an oxygen octahedral site, and exists in an oxygen tetrahedral site is  $0 < x \leq 0.33$ .

[0023] It becomes [ the single phase structure of Spinel structure is not acquired, or the elution volume of Mn to the inside of the organic electrolytic solution becomes large, and / when larger than this range / charge-and-discharge capacity ] small preferably, and is not desirable when the total amount of Li is less than one.

[0024] this -- in the case of  $0 \leq x \leq 0.15$ , a large capacity can be taken, and Mn elution volume is stopped low, and the value of x is especially desirable

[0025] Cr is desirable when the number of elements other than Li of this invention and Mn is one.

[0026] When an other type element is Cr, the empirical formula is as follows.

[0027] {Li} [Lix-Mn<sub>2-x-y</sub>-Cry] O<sub>4+d</sub> (however, { } -- inside -- the oxygen tetrahedral site in structure, and [] -- inside expresses the oxygen octahedral site in structure)  $0 < x \leq 0.33$ ,  $0 < y \leq 1.0$ ,  $-0.5 < d < 0.8$

In this case, it is desirable that it is  $0 < x \leq 0.15$  and  $0.02 \leq y \leq 0.2$ . Furthermore, other type elements other than Li and Mn are expressed with the following formula when it contains two sorts (M (1), M (2)).

[0028] Lix-Mn<sub>2-x-y1-y2</sub>, M(1) y<sub>1</sub>, and {Li} [M(2) y<sub>2</sub>] O<sub>4+d</sub> (however, { } -- inside -- the oxygen tetrahedral site in structure, and [] -- inside expresses the oxygen octahedral site in structure)  $0 < x \leq 0.33$ ,  $0 < y_1 + y_2 \leq 1.0$ ,  $-0.5 < d < 0.8$ , M (1), and M (2) are elements other than Li and Mn.

It is desirable that one sort [ of the other type element to contain ] M (1) is Cr, and, as for M (2), it is desirable that it is a \*\*\*\* metal.

[0029] It is more desirable that M (1) is Cr among the other type elements to contain, and M (2) is especially Fe,

and it is expressed with the following formula in that case.

[0030]  $\{Li\}$  [Lix-Cry1, Fey2, and Mn2-x-y1-y2] O4+d (however,  $\{ \}$  -- inside -- the oxygen tetrahedral site in structure, and  $[ ]$  -- inside expresses the oxygen octahedral site in structure)  $0 < x \leq 0.33$ ,  $0 < y1 \leq 0.5$ ,  $0 < y2 \leq 0.5$ ,  $-0.5 < d < 0.8$

In this empirical formula, it is desirable that it is  $0 < x \leq 0.15$ ,  $0 < y1 \leq 0.2$ , and  $0 < y2 \leq 0.2$ .

[0031] When content Spinel structure lithium manganese system oxides are Li, Mn, and a Spinel structure lithium manganese system oxide that contains at least one kind of other type elements other than Li and Mn (M) further and use Li for the oxygen tetrahedral site in structure for the other type element of this invention further as mentioned above at a cell active material or Li adsorption material at an oxygen octahedral site, it has the particulate structure which becomes highly efficient.

[0032] A content Spinel structure lithium manganese system oxide can carry out the manufacture method of the other type element of the above-mentioned this invention by mixing a manganese compound, a lithium compound, and the compound of a content other type element, and calcinating.

[0033] Be [ what is necessary / just although the compound to mix can generate an oxide below with burning temperature in an oxide a hydroxide, an oxidization hydroxide, a carbonate, a chloride salt, a nitrate, a sulfate, etc. ], especially an oxide, a hydroxide, an oxidization hydroxide, and a carbonate are desirable from the influence which it has to the environment of reactivity and waste gas.

[0034] It is indispensable to use the manganic acid ghost whose diameter of an average floc is 0.5-50 micrometers as a raw material manganese compound, and it is desirable to use that whose forming density of the raw material manganese compound is three or more 2.7 g/cm.

[0035] Since it is difficult to obtain what satisfies the fine-particles property of the Spinel structure lithium manganese system oxide containing the other type element of this invention, it is not desirable to use the manganic acid ghost besides this range.

[0036] It is desirable to use Na furthermore contained in a raw material manganese compound and the thing whose amount of K is 500 ppm or less, and when there were many these Na and amounts of K and a product is used for a cell active material, it is difficult to create highly efficient Li rechargeable battery.

[0037] In the manufacture method of the Spinel structure lithium manganese system oxide containing the other type element of this invention, it is desirable to use the lithium compound whose BET specific surface area is more than 1m<sup>2</sup>/g as a raw material lithium compound.

[0038] If a carbonate, a nitrate, a chloride salt, a hydroxide, an oxide, etc. are illustrated as a lithium compound and the lithium carbonate especially whose BET specific surface area is more than 1m<sup>2</sup>/g is used, also in the atmosphere, the Spinel structure lithium manganese system oxide which contains a uniform other type element easily can be manufactured, and it is very desirable.

[0039] Burning temperature [ in / manufacture of a content Spinel structure lithium manganese system oxide / for the other type element of this invention ] is suitably chosen so that a desired fine-particles property may be acquired from the range of 500-1000 degrees C.

[0040] burning temperature -- this -- it is hard to become the range of the request of the BET specific surface area and/or the diameter of a primary particle of a product by being out of range and is not desirable

[0041] Although both the inside of the atmosphere and the oxygen rich atmosphere of the atmosphere at the time of baking are usable, the ease of the structure of a firing furnace to the inside of the atmosphere is desirable.

[0042] In the aforementioned manufacture conditions, especially the thing for which the method shown below is adopted is desirable.

[0043] 1. How to calcinate, after mixing manganese compound, lithium compound, and compound of other type element and corning.

[0044] 2. How to calcinate, after calcinating, mixing lithium compound and/or compound of content other type element and corning [ mixture, a granulation, and ] manganese compound and lithium compound.

[0045] 3. Calcinate after mixing any one sort of a manganese compound, a lithium compound, and the compound of a content other type element after calcinating, mixture, a granulation, and, and corning a manganese compound, a lithium compound, and the compound of a content other type element.

[0046] Furthermore, if it can be made homogeneity when mixing a raw material, it is also suitable to calcinate being able to adopt any methods of the usual method and mixing like rotary kiln.

[0047] As for the manufactured Spinel structure lithium manganese system oxide, it is desirable to perform trituration and a classification timely.

[0048] In this invention, Li rechargeable battery using the Spinel structure lithium manganese system oxide manufactured as mentioned above as a positive active material was produced.

[0049] The matter which can occlusion emit a metal lithium and a lithium, or a lithium ion can be used for the negative-electrode active material used with the lithium secondary battery of this invention. For example, a metal lithium, a lithium / aluminium alloy, a lithium / tin alloy, a lithium/lead alloy, and the carbon system material

electrochemically inserted and desorbed from a lithium ion are illustrated, and insertion and the carbon system material which carries out \*\*\*\* are electrochemically suitable especially from the field of safety and the property of a cell in a lithium ion.

[0050] Moreover, as an electrolyte used with the lithium secondary battery of this invention, although there is especially no limit, it can use what dissolved lithium salt, and the solid electrolyte of lithium ion conductivity into organic solvents, such as carbonate, sulfolanes, lactone, and ether, for example.

[0051] The Spinel structure lithium manganese system oxide of this invention was used for the positive active material, and the cell shown in drawing 1 was constituted.

[0052] The lead wire for 1:positive electrodes, the mesh for 2:positive-electrode current collection, 3:positive electrode, 4:separator, 5:negative electrode, the mesh for 6:negative-electrode current collection, the lead wire for 7:negative electrodes, and 8:container are shown all over drawing.

[0053] In this invention, a stable highly efficient lithium secondary battery can be obtained using the positive active material, the negative-electrode active material, and lithium salt content nonaqueous electrolyte which have been described above.

[0054] Although an example is described below, this invention is not limited to this.

[0055]

[Example] Each measurement in the example and the example of comparison of this invention was carried out on condition that the following.

[0056] - The XRD pattern was measured on condition that the following.

[0057]

Measurement model : Mac Saiensu-Sha Co., Ltd. MXP-3 irradiation X-ray : Cu K alpha-rays measurement mode : Step scan scan conditions: Per second 0.04-degree measurement time : 3-second measuring range : 80 degrees and the component analysis were performed by the ICP spectroscopy from 5 times as 2theta.

[0058] - The degree of oxidization of Mn element was performed by the oxalic acid method.

[0059] As "composition of Spinel structure lithium manganese system oxide" example, and an example of comparison, it compounded by the following methods.

[0060] Cr is used as an example 1 - a 5 other-type element M. MnO<sub>2</sub> (electrolytic manganese dioxide by TOSOH CORP.) whose diameter of an average floc is 20 micrometers, the lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) whose BET specific surface area is 3m<sup>2</sup>/g, and the chrome oxide (Cr 2O<sub>3</sub>) whose diameter of an average floc is 1 micrometer change the ratio of Cr and Mn. After having carried out weighing capacity of the amount of Li(s) in the following empirical formulas so that the value of x might become fixed by 0.06 (Li:(Li+Mn+Cr)=1.06:3.00), a mortar may be used, mixing and carrying out temporary quenching at 450 degrees C for 24 hours, it calcinated at 750 degrees C for 24 hours.

[0061]

The photograph which observed the particulate structure of the Spinel structure lithium manganese system oxide obtained in the Li<sub>0.06</sub> and {Li} [Cry-Mn(2-0.06-y)] O<sub>4</sub> example 3 by one 20,000 times the scale factor of this using SEM is shown in drawing 2.

[0062] It became clear from this drawing that all the diameters of a particle primary particle of the Spinel structure lithium manganese system oxide obtained in the example 3 are 1 micrometer or less, and the first [ an average of ] particle diameter is 1 micrometer or less.

[0063] Moreover, it presumed that the structure of the obtained Spinel structure lithium manganese system oxide was the above-mentioned chemical formula by the lattice constant value and Rietveld analysis by the X diffraction.

[0064] In example 6 example 3, the last burning temperature was made the same from 750 degrees C except having made it high at 900 degrees C.

[0065] The photograph which observed the particulate structure of the obtained Spinel structure lithium manganese system oxide by one 20,000 times the scale factor of this using SEM is shown in drawing 3.

[0066] The diameter of a primary particle of the obtained Spinel structure lithium manganese system oxide became clear [ the thing of the particle diameter / first / an average of ] which is included also for a particle 1 micrometers or more and which is 3 micrometers or less / from this drawing, although it was.

[0067] Except that the amount of Li(s) was made for the value of x to be set to 0.02 in example 7 example 4, it was presupposed that it is the same.

[0068] It was presupposed except having used Co instead of Cr in eight to example 10 examples 2-4 that it is the same.

[0069] In addition, Co raw material used basic cobalt carbonate.

[0070] It was presupposed except having used nickel instead of Cr in 11 to example 13 examples 2-4 that it is the same.

[0071] In addition, nickel raw material used basic nickel carbonate.

[0072] It was presupposed except having used Fe instead of Cr in 14 to example 16 examples 2-4 that it is the same.

[0073] In addition, Fe raw material used Fe 3O<sub>4</sub>.

[0074] As an other type element M1 of the example 17 first, carry out Fe use as second other type element M2, and Cr is set to the following empirical formula. The value of x the amount of Li(s) 0.01 (Li:(Li+Mn+Cr+Fe)=1.01:3.00), The value of y1 carries out weighing capacity of Cr 2O<sub>3</sub> which are MnO<sub>2</sub> whose diameter of a floc is 20 micrometers so that the value of 0.1 and y2 may be set to 0.1, Li<sub>2</sub>CO<sub>3</sub> whose BET specific surface area is 3m<sup>2</sup>/g, and 1 micrometer of diameters of an average floc, and Fe<sub>3</sub>O<sub>4</sub>. The mortar could be used, and after mixing and carrying out temporary quenching at 450 degrees C for 24 hours, it calcinated at 750 degrees C for 24 hours. After having carried out weighing capacity of MnO<sub>2</sub> (electrolytic manganese dioxide by TOSOH CORP.) whose diameter of Li0.01, Cr0.1, Fe0.1, and example of {Li} [Mn1.79] O<sub>4</sub> comparison 1 floc is 20 micrometers, and the lithium carbonate whose BET specific surface area is 3m<sup>2</sup>/g so that it might be set to x= 0.0 (Li:Mn=1.00:2.0), a mortar may be used, mixing and carrying out temporary quenching at 450 degrees C for 24 hours, it calcinated at 750 degrees C for 24 hours.

[0075] The product showed the same pattern as LiMn 2O<sub>4</sub> of the JCPDS card 35-782.

[0076] It carried out on the same conditions as the example 1 of comparison except having been referred to as x= 0.06 (Li:Li+Mn=1.06:3.0) in the example 1 of example of comparison 2 comparison.

[0077] It carried out on the same conditions as the example 1 of comparison except having been referred to as x= 0.10 (Li:Li+Mn=1.10:3.0) in the example 1 of example of comparison 3 comparison.

[0078] It mixed so that it might be set to example of comparison 4 Li:Cr:Mn=0.95:0.2:1.80, and it calcinated on condition that the example 1 of comparison.

[0079] The product of an example and the example of comparison was cubic Spinel structure single phase except example of comparison 4.

[0080] It sank into 15ml of electrolytic solutions which dissolved [ the lithium manganese system oxide produced in "Mn elution test" example and the example of comparison ] each the 6 fluoride [ phosphoric-acid ] lithium for 3g in the mixed solvent of ethylene carbonate and dimethyl carbonate by the concentration of one mol / dm<sup>3</sup>, and the 85 degrees C of the amounts of Mn after holding for 100 hours and in the electrolytic solution were analyzed by the ICP spectroscopy.

[0081] The result was shown in Table 1.

[0082]

[Table 1]

	L i 量 (x)	他種元素		M n 溶出量 (mol%)	格子定数 (Å)	B E T (m <sup>2</sup> /g)	初期容量 (mAh/g)	容量維持率(%) 室温 50℃	溶出試験維持率 (%)
		M	y						
実施例 1	0.06	Cr	0.01	0.65	8.237	1.75	120	-- --	--
実施例 2	0.06	Cr	0.02	0.49	8.235	1.58	120	-- --	--
実施例 3	0.06	Cr	0.1	0.09	8.230	2.31	108	99 94	90
実施例 4	0.06	Cr	0.2	0.11	8.223	1.83	94	99 95	95
実施例 5	0.06	Cr	0.4	0.14	8.209	1.80	63	97 95	95
実施例 6	0.06	Cr	0.1	0.07	8.237	0.90	103	99 94	90
実施例 7	0.02	Cr	0.2	0.20	8.242	2.11	115	95 90	85
実施例 8	0.06	Co	0.02	0.64	8.231	1.41	120	-- --	--
実施例 9	0.06	Co	0.1	0.52	8.228	1.60	108	96 91	81
実施例 10	0.06	Co	0.2	0.49	8.196	1.43	93	96 92	85
実施例 11	0.06	Ni	0.02	0.62	8.234	1.56	117	-- --	--
実施例 12	0.06	Ni	0.1	0.23	8.219	1.73	93	95 92	88
実施例 13	0.06	Ni	0.2	0.13	8.202	1.66	63	96 92	90
実施例 14	0.06	Fe	0.02	0.49	8.235	1.68	120	90 88	81
実施例 15	0.06	Fe	0.1	0.31	8.237	2.11	108	92 90	85
実施例 16	0.06	Fe	0.2	0.18	8.234	2.12	93	99 95	96
実施例 17	0.01	Cr	0.1	0.05	8.239	1.88	107	99 95	94
		Fe	0.1						
比較例 1	1.00	--	0.0	1.06	8.242	1.80	130	90 60	60
比較例 2	1.06	--	0.0	0.84	8.234	1.75	123	94 83	75
比較例 3	1.10	--	0.0	0.83	8.219	1.62	106	95 84	76
比較例 4	0.95	Cr	0.2	0.95	---	1.70	---	-- --	--

[0083] The cell examination was performed using the sample after the lithium manganese system oxide obtained in "composition of cell" example, and the example of comparison, and the aforementioned Mn elution test. The cell examination mixed a sample, the polytetrafluoroethylene of an electric conduction agent, and the mixture (tradename : TAB- 2) of acetylene black at a rate of 2:1 by the weight ratio. After fabricating mixture by the pressure of 1 ton/cm<sup>2</sup> in the shape of a pellet on a mesh (SUS 316), reduced pressure drying of it was carried out at [http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web.cgi\\_ejje](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web.cgi_ejje)

200 degrees C for 24 hours.

[0084] Thus, use the obtained pellet for the positive electrode of 3 of drawing 1 , and the piece of a lithium clipped out from the lithium foil (0.2mm in thickness) is used for the negative electrode of 5 of drawing 1 . The solution which dissolved the 6 fluoride [ phosphoric-acid ] lithium in the electrolytic solution by the concentration of one mol / dm<sup>3</sup> at the mixed solvent of propylene carbonate and diethyl carbonate is infiltrated into the separator of 4 of drawing 1 . Moreover, the cell which showed the lithium ion electrochemically to the negative electrode at drawing 1 using the carbon system material from which it is inserted and desorbed was constituted.

[0085] The lithium manganese system oxide produced in "evaluation of cell property" example and the example of comparison was used for the positive active material, the cell was produced, and the cell voltage repeatedmA [ of charges and discharges / 1.0 / / ] between 4.5V and 3.5V with the fixed current of 2 cm.

[0086] The test temperature was carried out at a room temperature and 50 degrees C.

[0087] Initial capacity, the capacity maintenance factor (% of the service capacity of 50 cycle eye to 10 cycle eye), and the elution test maintenance factor (% to the initial capacity in front of the elution test of the capacity after an elution test) were shown in Table 1.

[0088]

[Effect of the Invention] The Spinel structure lithium manganese system oxide of this invention has little Mn elution in an organic solvent, and even if it demonstrates the charge-and-discharge cycle nature stabilized by after the mothball and performs charge and discharge at an elevated temperature further, it has little degradation.

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TECHNICAL FIELD

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[The technical field to which invention belongs] this invention relates to the Spinel structure lithium manganese system oxide containing other type elements other than Li and Mn (M), and its manufacture method list use.

[0002] A manganic acid ghost is a material used for many years as a cell active material. The lithium manganic acid ghost which is the quality of a composite of manganese and a lithium, and the lithium manganese system oxide which replaced some manganese of this lithium manganic acid ghost by the other type element are material which attracts attention in recent years as a positive active material of a lithium secondary battery which can attain high power and high-energy density.

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PRIOR ART

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[Description of the Prior Art] It is called for that the positive-electrode material for lithium secondary batteries has high that a voltage operating space is high, that it is high service capacity, and cycle stability, and the multiple oxide of \*\*, such as Li and various metals, for example, Co, nickel, Mn, etc., is examined.

[0004] If it is known that the two-step electric discharge with a flat part portion is shown and the 4V neighborhood and the 3V neighborhood can be made to carry out the cycle of  $\text{LiMn}_2\text{O}_4$  of the Spinel structure which is a kind of the multiple oxide of Li and Mn in reversible by the operating space of the 4V neighborhood at the time of electric discharge, since it can expect taking out high energy, it is thought that it is promising as a positive active material.

[0005] However, when Mn in  $\text{LiMn}_2\text{O}_4$  structure performed charge and discharge as a lithium secondary battery positive electrode, it turns out that it is eluted in the organic electrolytic solution in recent years. Furthermore, in the experiment of this invention persons, it was based on the kind of electrolytic-solution system, and having saved  $\text{LiMn}_2\text{O}_4$  at 85 degrees C in the organic electrolytic solution, even if it did not perform charge and discharge also turned out that the amount of Mn in structure was eluted also about 1mol%, and the property as a positive-electrode material fell remarkably after elution.

[0006] When  $\text{LiMn}_2\text{O}_4$  was used as a positive electrode for lithium secondary batteries, even if it did not perform charge and discharge, it only saved for a long period of time, and Mn in structure is eluted in the organic electrolytic solution, and this shows possibility of stopping operating as a positive electrode for lithium secondary batteries.

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EFFECT OF THE INVENTION

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[Effect of the Invention] The Spinel structure lithium manganese system oxide of this invention has little Mn elution in an organic solvent, and even if it demonstrates the charge-and-discharge cycle nature stabilized by after the mothball and performs charge and discharge at an elevated temperature further, it has little degradation.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the highly efficient lithium secondary battery which used for the positive electrode the highly efficient Spinel structure lithium manganese system oxide and this lithium manganese system oxide which suppressed Mn elution in the organic electrolytic solution as a positive-electrode material for Li rechargeable batteries.

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MEANS

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[Means for Solving the Problem] As a result of this invention persons' inquiring wholeheartedly, it was expressed with the following composition and the Spinel structure lithium manganese system oxide containing variety elements other than Li and Mn found out that the above-mentioned purpose could be attained.

[0009]

{Li} [Lix-My-Mn(2-x-y)] O<sub>4+d</sub> (however, {} -- inside -- the oxygen tetrahedral site in structure (8a site), and [] -- inside expresses the oxygen octahedral site in structure (16d site))  $0 < x \leq 0.33$ ,  $0 < y \leq 1.0$ ,  $-0.5 < d < 0.8$ .

[0010] If a firing environments is a reducing atmosphere, this d value will turn into a value of minus, and will turn into a value of plus in an oxidizing atmosphere. M is elements other than Li and Mn.

[0011] Furthermore, the highly efficient lithium secondary battery using the Spinel structure lithium manganese system oxide containing the manufacture method of the Spinel structure lithium manganese system oxide containing Li of this invention and other type elements other than Mn (M), Li of this invention, and other type elements other than Mn (M) as a positive active material was found out, and this invention was completed.

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## OPERATION

[Function] Hereafter, this invention is explained concretely.

[0013] The Spinel structure lithium manganese system oxides containing Li of this invention and other type elements other than Mn (M) are the following composition.

[0014]

{Li} [Lix-My-Mn(2-x-y)] O<sub>4+d</sub> (however, {} -- inside -- the oxygen tetrahedral site in structure, and [] -- inside expresses the oxygen octahedral site in structure)  $0 < x \leq 0.33$ ,  $0 < y \leq 1.0$ ,  $-0.5 < d < 0.8$ , and M are elements other than Li and Mn.

It exists in the oxygen tetrahedral site in structure, the crystal structure is cubic Spinel structure as a product, and, as for these M elements, what forms the Spinel structure lithium manganese system oxide the lattice constant a of whose is 8.19Å or more and 8.24Å or less is desirable.

[0015] In addition, the energy taken out when action potential becomes low and constitutes Li rechargeable battery as Spinel structure other than a cubic, although there was a tetragonal phase etc. becomes small and is not desirable.

[0016] moreover, the lattice constant a -- the above -- if it becomes out of range, since the manganese in the structure will become unstable, Mn elution volume becomes large and is not desirable

[0017] These M elements are at least one sort of elements chosen from the group of Be, Mg, calcium, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Fe, Co, nickel, Cu, Ag, Zn, B, aluminum, Ga, In, Si, germanium, Sn, Pb, P, As, Sb, and Bi.

[0018] It is desirable that the diameter of an average floc of the Spinel structure lithium manganese system oxide which furthermore contains the other type element of this invention is 1-50 micrometers, and a BET specific surface area is 0.1-5m<sup>2</sup>/g.

[0019] When the diameter of an average floc is larger than this range, or when a BET specific surface area is smaller than this range An elevated temperature is required for manufacture, and since a high performance is hard to be obtained when it is used for a cell active material, are not desirable. Conversely, when the diameter of an average floc is smaller than this range, or when a BET specific surface area is larger than this range and it uses it for a cell active material, restoration nature is bad, and the problem of Mn tending to be eluted out of structure is easy to be generated and is not desirable.

[0020] Moreover, as for the first [ an average of ] particle diameter of the Spinel structure lithium manganese system oxide containing the other type element of this invention, it is desirable that it is 3 micrometers or less. Since a high performance is hard to be obtained when larger [ than this range ] and it is used for a cell active material etc., it is not desirable.

[0021] y showing the amount of the other type element of the Spinel structure lithium manganese system oxide containing the other type element of this invention is [ ... It is  $y_n \leq 1.0$ . ] the content of each other type element, when it is  $0 < y \leq 1.0$  and contains two or more sorts of other type elements y<sub>1</sub>, y<sub>2</sub>, and y<sub>3</sub> ... It is referred to as y<sub>n</sub> and is  $0 < y_1 + y_2 + y_3 +$ .

[0022] this -- charge-and-discharge capacity of the total amount of y decreases, and it is not desirable at 1.0 or more The amount x which exists in the oxygen octahedral site at the time of setting to 1 the amount which Li in the Spinel structure lithium manganese system oxide containing the other type element of this invention exists in both the oxygen tetrahedral site in structure and an oxygen octahedral site, and exists in an oxygen tetrahedral site is  $0 < x \leq 0.33$ .

[0023] It becomes [ the single phase structure of Spinel structure is not acquired, or the elution volume of Mn to the inside of the organic electrolytic solution becomes large, and / when larger than this range / charge-and-discharge capacity ] small preferably, and is not desirable when the total amount of Li is less than one.

[0024] this -- in the case of  $0 \leq x \leq 0.15$ , a large capacity can be taken, and Mn elution volume is stopped low, and the value of x is especially desirable

[0025] Cr is desirable when the number of elements other than Li of this invention and Mn is one.

[0026] When an other type element is Cr, the empirical formula is as follows.

[0027] {Li} [Lix-Mn2-x-y-Cry] O4+d (however, {} -- inside -- the oxygen tetrahedral site in structure, and [] -- inside expresses the oxygen octahedral site in structure)  $0 < x \leq 0.33$ ,  $0 < y \leq 1.0$ ,  $-0.5 < d < 0.8$

In this case, it is desirable that it is  $0 < x \leq 0.15$  and  $0.02 \leq y \leq 0.2$ . Furthermore, other type elements other than Li and Mn are expressed with the following formula when it contains two sorts (M (1), M (2)).

[0028] Lix-Mn2-x-y1-y2, M(1) y1, and {Li} [M(2) y2] O4+d (however, {} -- inside -- the oxygen tetrahedral site in structure, and [] -- inside expresses the oxygen octahedral site in structure)  $0 < x \leq 0.33$ ,  $0 < y1 + y2 \leq 1.0$ ,  $-0.5 < d < 0.8$ , M (1), and M (2) are elements other than Li and Mn.

It is desirable that one sort [ of the other type element to contain ] M (1) is Cr, and, as for M (2), it is desirable that it is a \*\*\*\* metal.

[0029] It is more desirable that M (1) is Cr among the other type elements to contain, and M (2) is especially Fe, and it is expressed with the following formula in that case.

[0030] {Li} [Lix-Cry1, Fey2, and Mn2-x-y1-y2] O4+d (however, {} -- inside -- the oxygen tetrahedral site in structure, and [] -- inside expresses the oxygen octahedral site in structure)  $0 < x \leq 0.33$ ,  $0 < y1 \leq 0.5$ ,  $0 < y2 \leq 0.5$ ,  $-0.5 < d < 0.8$

In this empirical formula, it is desirable that it is  $0 < x \leq 0.15$ ,  $0 < y1 \leq 0.2$ , and  $0 < y2 \leq 0.2$ .

[0031] When content Spinel structure lithium manganese system oxides are Li, Mn, and a Spinel structure lithium manganese system oxide that contains at least one kind of other type elements other than Li and Mn (M) further and use Li for the oxygen tetrahedral site in structure for the other type element of this invention further as mentioned above at a cell active material or Li adsorption material at an oxygen octahedral site, it has the particulate structure which becomes highly efficient.

[0032] A content Spinel structure lithium manganese system oxide can carry out the manufacture method of the other type element of the above-mentioned this invention by mixing a manganese compound, a lithium compound, and the compound of a content other type element, and calcinating.

[0033] Be [ what is necessary / just although the compound to mix can generate an oxide below with burning temperature in an oxide a hydroxide, an oxidization hydroxide, a carbonate, a chloride salt, a nitrate, a sulfate, etc. ], especially an oxide, a hydroxide, an oxidization hydroxide, and a carbonate are desirable from the influence which it has to the environment of reactivity and waste gas.

[0034] It is indispensable to use the manganic acid ghost whose diameter of an average floc is 0.5-50 micrometers as a raw material manganese compound, and it is desirable to use that whose forming density of the raw material manganese compound is three or more 2.7 g/cm.

[0035] Since it is difficult to obtain what satisfies the fine-particles property of the Spinel structure lithium manganese system oxide containing the other type element of this invention, it is not desirable to use the manganic acid ghost besides this range.

[0036] It is desirable to use Na furthermore contained in a raw material manganese compound and the thing whose amount of K is 500 ppm or less, and when there were many these Na and amounts of K and a product is used for a cell active material, it is difficult to create highly efficient Li rechargeable battery.

[0037] In the manufacture method of the Spinel structure lithium manganese system oxide containing the other type element of this invention, it is desirable to use the lithium compound whose BET specific surface area is more than 1m2/g as a raw material lithium compound.

[0038] If a carbonate, a nitrate, a chloride salt, a hydroxide, an oxide, etc. are illustrated as a lithium compound and the lithium carbonate especially whose BET specific surface area is more than 1m2/g is used, also in the atmosphere, the Spinel structure lithium manganese system oxide which contains a uniform other type element easily can be manufactured, and it is very desirable.

[0039] Burning temperature [ in / manufacture of a content Spinel structure lithium manganese system oxide / for the other type element of this invention ] is suitably chosen so that a desired fine-particles property may be acquired from the range of 500-1000 degrees C.

[0040] burning temperature -- this -- it is hard to become the range of the request of the BET specific surface area and/or the diameter of a primary particle of a product by being out of range and is not desirable

[0041] Although both the inside of the atmosphere and the oxygen rich atmosphere of the atmosphere at the time of baking are usable, the ease of the structure of a firing furnace to the inside of the atmosphere is desirable.

[0042] In the aforementioned manufacture conditions, especially the thing for which the method shown below is adopted is desirable.

[0043] 1. How to calcinate, after mixing manganese compound, lithium compound, and compound of other type element and corning.

[0044] 2. How to calcinate, after calcinating, mixing lithium compound and/or compound of content other type element and corning [ mixture, a granulation, and ] manganese compound and lithium compound.

[0045] 3. Calcinate after mixing any one sort of a manganese compound, a lithium compound, and the compound of a content other type element after calcinating, mixture, a granulation, and, and corning a manganese compound, a lithium compound, and the compound of a content other type element.

[0046] Furthermore, if it can be made homogeneity when mixing a raw material, it is also suitable to calcinate being able to adopt any methods of the usual method and mixing like rotary kiln.

[0047] As for the manufactured Spinel structure lithium manganese system oxide, it is desirable to perform trituration and a classification timely.

[0048] In this invention, Li rechargeable battery using the Spinel structure lithium manganese system oxide manufactured as mentioned above as a positive active material was produced.

[0049] The matter which can occlusion emit a metal lithium and a lithium, or a lithium ion can be used for the negative-electrode active material used with the lithium secondary battery of this invention. For example, a metal lithium, a lithium / aluminium alloy, a lithium / tin alloy, a lithium/lead alloy, and the carbon system material electrochemically inserted and desorbed from a lithium ion are illustrated, and insertion and the carbon system material which carries out \*\*\*\* are electrochemically suitable especially from the field of safety and the property of a cell in a lithium ion.

[0050] Moreover, as an electrolyte used with the lithium secondary battery of this invention, although there is especially no limit, it can use what dissolved lithium salt, and the solid electrolyte of lithium ion conductivity into organic solvents, such as carbonate, sulfolanes, lactone, and ether, for example.

[0051] The Spinel structure lithium manganese system oxide of this invention was used for the positive active material, and the cell shown in drawing 1 was constituted.

[0052] The lead wire for 1:positive electrodes, the mesh for 2:positive-electrode current collection, 3:positive electrode, 4:separator, 5:negative electrode, the mesh for 6:negative-electrode current collection, the lead wire for 7:negative electrodes, and 8:container are shown all over drawing.

[0053] In this invention, a stable highly efficient lithium secondary battery can be obtained using the positive active material, the negative-electrode active material, and lithium salt content nonaqueous electrolyte which have been described above.

[0054] Although an example is described below, this invention is not limited to this.

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## EXAMPLE

[Example] Each measurement in the example and the example of comparison of this invention was carried out on condition that the following.

[0056] - The XRD pattern was measured on condition that the following.

[0057]

Measurement model : Mac Saiensu-Sha Co., Ltd. MXP-3 irradiation X-ray : Cu K alpha-rays measurement mode : Step scan scan conditions: Per second 0.04-degree measurement time : 3-second measuring range : 80 degrees and the component analysis were performed by the ICP spectroscopy from 5 times as 2theta.

[0058] - The degree of oxidization of Mn element was performed by the oxalic acid method.

[0059] As "composition of Spinel structure lithium manganese system oxide" example, and an example of comparison, it compounded by the following methods.

[0060] Cr is used as an example 1 - a 5 other-type element M. MnO<sub>2</sub> (electrolytic manganese dioxide by TOSOH CORP.) whose diameter of an average floc is 20 micrometers, the lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) whose BET specific surface area is 3m<sup>2</sup>/g, and the chrome oxide (Cr<sub>2</sub>O<sub>3</sub>) whose diameter of an average floc is 1 micrometer change the ratio of Cr and Mn. After having carried out weighing capacity of the amount of Li(s) in the following empirical formulas so that the value of x might become fixed by 0.06 (Li:(Li+Mn+Cr)=1.06:3.00), a mortar may be used, mixing and carrying out temporary quenching at 450 degrees C for 24 hours, it calcinated at 750 degrees C for 24 hours.

[0061]

The photograph which observed the particulate structure of the Spinel structure lithium manganese system oxide obtained in the Li<sub>0.06</sub> and {Li} [Cry-Mn(2-0.06-y)] O<sub>4</sub> example 3 by one 20,000 times the scale factor of this using SEM is shown in drawing 2.

[0062] It became clear from this drawing that all the diameters of a particle primary particle of the Spinel structure lithium manganese system oxide obtained in the example 3 are 1 micrometer or less, and the first [ an average of ] particle diameter is 1 micrometer or less.

[0063] Moreover, it presumed that the structure of the obtained Spinel structure lithium manganese system oxide was the above-mentioned chemical formula by the lattice constant value and Rietveld analysis by the X diffraction.

[0064] In example 6 example 3, the last burning temperature was made the same from 750 degrees C except having made it high at 900 degrees C.

[0065] The photograph which observed the particulate structure of the obtained Spinel structure lithium manganese system oxide by one 20,000 times the scale factor of this using SEM is shown in drawing 3.

[0066] The diameter of a primary particle of the obtained Spinel structure lithium manganese system oxide became clear [ the thing of the particle diameter / first / an average of ] which is included also for a particle 1 micrometers or more and which is 3 micrometers or less / from this drawing, although it was.

[0067] Except that the amount of Li(s) was made for the value of x to be set to 0.02 in example 7 example 4, it was presupposed that it is the same.

[0068] It was presupposed except having used Co instead of Cr in eight to example 10 examples 2-4 that it is the same.

[0069] In addition, Co raw material used basic cobalt carbonate.

[0070] It was presupposed except having used nickel instead of Cr in 11 to example 13 examples 2-4 that it is the same.

[0071] In addition, nickel raw material used basic nickel carbonate.

[0072] It was presupposed except having used Fe instead of Cr in 14 to example 16 examples 2-4 that it is the same.

[0073] In addition, Fe raw material used Fe<sub>3</sub>O<sub>4</sub>.

[0074] As an other type element M1 of the example 17 first, carry out Fe use as second other type element M2, and Cr is set to the following empirical formula. The value of x the amount of Li(s) 0.01 (Li:(Li+Mn+Cr+Fe)

=1.01:3.00), The value of y1 carries out weighing capacity of Cr 2O<sub>3</sub> which are MnO<sub>2</sub> whose diameter of a floc is 20 micrometers so that the value of 0.1 and y2 may be set to 0.1, Li<sub>2</sub>CO<sub>3</sub> whose BET specific surface area is 3m<sup>2</sup>/g, and 1 micrometer of diameters of an average floc, and Fe<sub>3</sub>O<sub>4</sub>. The mortar could be used, and after mixing and carrying out temporary quenching at 450 degrees C for 24 hours, it calcinated at 750 degrees C for 24 hours. After having carried out weighing capacity of MnO<sub>2</sub> (electrolytic manganese dioxide by TOSOH CORP.) whose diameter of Li<sub>0.01</sub>, Cr<sub>0.1</sub>, Fe<sub>0.1</sub>, and example of {Li} [Mn<sub>1.79</sub>] O<sub>4</sub> comparison 1 floc is 20 micrometers, and the lithium carbonate whose BET specific surface area is 3m<sup>2</sup>/g so that it might be set to x= 0.0 (Li:Mn=1.00:2.0), a mortar may be used, mixing and carrying out temporary quenching at 450 degrees C for 24 hours, it calcinated at 750 degrees C for 24 hours.

[0075] The product showed the same pattern as LiMn 2O<sub>4</sub> of the JCPDS card 35-782.

[0076] It carried out on the same conditions as the example 1 of comparison except having been referred to as x= 0.06 (Li:Li+Mn=1.06:3.0) in the example 1 of example of comparison 2 comparison.

[0077] It carried out on the same conditions as the example 1 of comparison except having been referred to as x= 0.10 (Li:Li+Mn=1.10:3.0) in the example 1 of example of comparison 3 comparison.

[0078] It mixed so that it might be set to example of comparison 4 Li:Cr:Mn=0.95:0.2:1.80, and it calcinated on condition that the example 1 of comparison.

[0079] The product of an example and the example of comparison was cubic Spinel structure single phase except example of comparison 4.

[0080] It sank into 15ml of electrolytic solutions which dissolved [ the lithium manganese system oxide produced in "Mn elution test" example and the example of comparison ] each the 6 fluoride [ phosphoric-acid ] lithium for 3g in the mixed solvent of ethylene carbonate and dimethyl carbonate by the concentration of one mol / dm<sup>3</sup>, and the 85 degrees C of the amounts of Mn after holding for 100 hours and in the electrolytic solution were analyzed by the ICP spectroscopy.

[0081] The result was shown in Table 1.

[0082]

[Table 1]

	L i 量 (x)	他種元素		M n 溶出量 (mol%)	格子定数 (Å)	B E T (m <sup>2</sup> /g)	初期容量 (mAh/g)	容量維持率(%)		溶出試験維持率 (%)
		M	y					室温	50℃	
実施例 1	0.06	Cr	0.01	0.65	8.237	1.75	120	--	--	--
実施例 2	0.06	Cr	0.02	0.49	8.235	1.58	120	--	--	--
実施例 3	0.06	Cr	0.1	0.09	8.230	2.31	108	99	94	90
実施例 4	0.06	Cr	0.2	0.11	8.223	1.83	94	99	95	95
実施例 5	0.06	Cr	0.4	0.14	8.209	1.80	63	97	95	95
実施例 6	0.06	Cr	0.1	0.07	8.237	0.90	103	99	94	90
実施例 7	0.02	Cr	0.2	0.20	8.242	2.11	115	95	90	85
実施例 8	0.06	Co	0.02	0.64	8.231	1.41	120	--	--	--
実施例 9	0.06	Co	0.1	0.52	8.228	1.60	108	96	91	81
実施例 10	0.06	Co	0.2	0.49	8.196	1.43	93	96	92	85
実施例 11	0.06	Ni	0.02	0.62	8.234	1.56	117	--	--	--
実施例 12	0.06	Ni	0.1	0.23	8.219	1.73	93	95	92	88
実施例 13	0.06	Ni	0.2	0.13	8.202	1.66	63	96	92	90
実施例 14	0.06	Fe	0.02	0.49	8.235	1.68	120	90	88	81
実施例 15	0.06	Fe	0.1	0.31	8.237	2.11	108	92	90	85
実施例 16	0.06	Fe	0.2	0.18	8.234	2.12	93	99	95	96
実施例 17	0.01	Cr	0.1	0.05	8.239	1.88	107	99	95	94
		Fe	0.1							
比較例 1	1.00	--	0.0	1.06	8.242	1.80	130	90	60	60
比較例 2	1.06	--	0.0	0.84	8.234	1.75	123	94	83	75
比較例 3	1.10	--	0.0	0.83	8.219	1.62	106	95	84	76
比較例 4	0.95	Cr	0.2	0.95	---	1.70	---	--	--	--

[0083] The cell examination was performed using the sample after the lithium manganese system oxide obtained in "composition of cell" example, and the example of comparison, and the aforementioned Mn elution test. The cell examination mixed a sample, the polytetrafluoroethylene of an electric conduction agent, and the mixture (tradename : TAB- 2) of acetylene black at a rate of 2:1 by the weight ratio. After fabricating mixture by the pressure of 1 ton/cm<sup>2</sup> in the shape of a pellet on a mesh (SUS 316), reduced pressure drying of it was carried out at 200 degrees C for 24 hours.

[0084] Thus, use the obtained pellet for the positive electrode of 3 of drawing 1 , and the piece of a lithium clipped out from the lithium foil (0.2mm in thickness) is used for the negative electrode of 5 of drawing 1 . The solution which dissolved the 6 fluoride [ phosphoric-acid ] lithium in the electrolytic solution by the concentration of one

mol / dm<sup>3</sup> at the mixed solvent of propylene carbonate and diethyl carbonate is infiltrated into the separator of 4 of drawing 1 . Moreover, the cell which showed the lithium ion electrochemically to the negative electrode at drawing 1 using the carbon system material from which it is inserted and desorbed was constituted.

[0085] The lithium manganese system oxide produced in "evaluation of cell property" example and the example of comparison was used for the positive active material, the cell was produced, and the cell voltage repeatedmA [ of charges and discharges / 1.0 / ] between 4.5V and 3.5V with the fixed current of 2 cm.

[0086] The test temperature was carried out at a room temperature and 50 degrees C.

[0087] Initial capacity, the capacity maintenance factor (% of the service capacity of 50 cycle eye to 10 cycle eye), and the elution test maintenance factor (% to the initial capacity in front of the elution test of the capacity after an elution test) were shown in Table 1.

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[Translation done.]



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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The cell which used the Spinel structure lithium manganese system oxide of this invention for the positive active material, and constituted it is shown.

[Description of Notations]

- 1: Lead wire for positive electrodes
- 2: Mesh for positive-electrode current collection
- 3: Positive electrode
- 4: Separator
- 5: Negative electrode
- 6: Mesh for negative-electrode current collection
- 7: Lead wire for negative electrodes
- 8: Container

[Drawing 2] It is the photograph in which the particulate structure of the Spinel structure lithium manganese system oxide obtained in the example 3 is shown.

[Drawing 3] It is the photograph in which the particulate structure of the Spinel structure lithium manganese system oxide obtained in the example 6 is shown.

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[Translation done.]

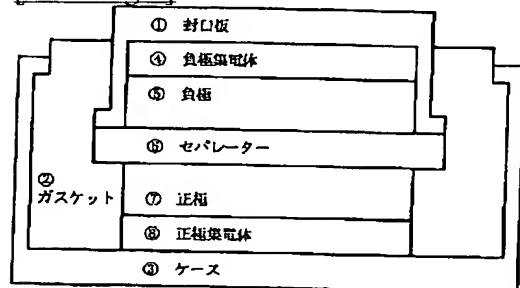
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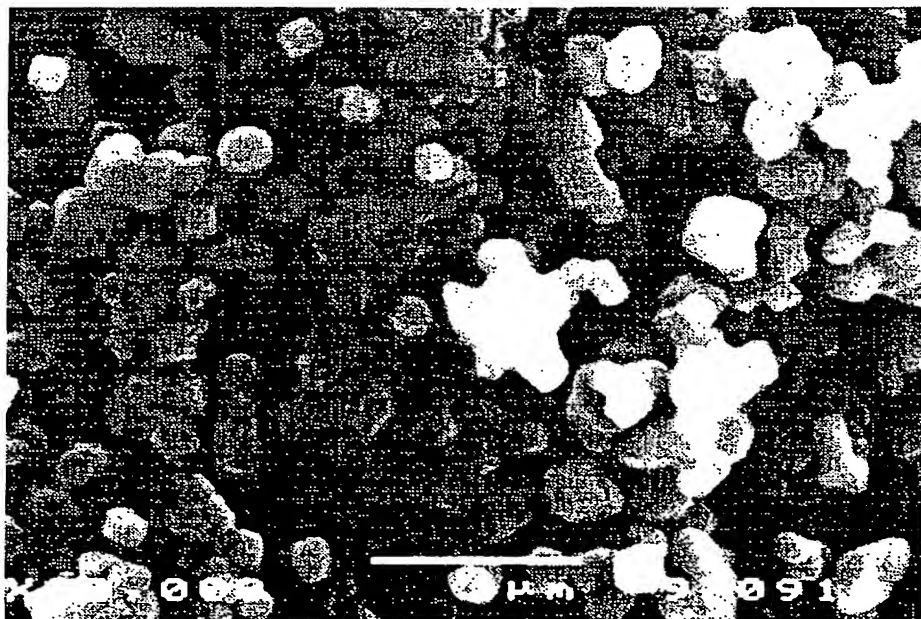
## DRAWINGS

[Drawing 1]



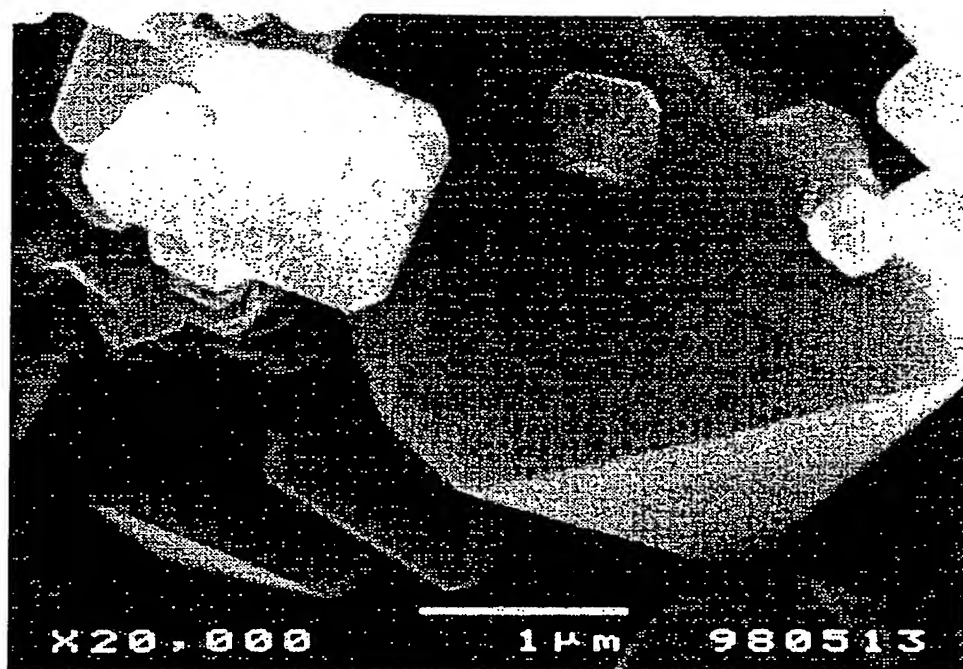
[Drawing 2]

図面代用写真



[Drawing 3]

図面代用写真



[Translation done.]